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bipyridyl in the title or abstract AND 1945:1974 as the publication date AND ICI as the applicant

Displaying selected publications

Publication	Title	Page
GB1268191 (A)	PROCESS FOR THE MANUFACTURE OF BIPYRI...	2
US3704238 (A)	PROCESS FOR PRODUCING 4,4'-BIPYRIDYL ...	3
US3598826 (A)	PRODUCTION OF 1,1'-ETHYLENE-1,1',2,2'...	4
GB1135682 (A)	Process for preparing bipyridylium co...	5
US3478042 (A)	PRODUCTION OF N:N-DISUBSTITUTED TETRA...	6
GB1119544 (A)	Production of n:n'-disubstituted bipy...	7
GB1136823 (A)	Production of alkali metal oxides	8
GB1074994 (A)	Production of bipyridylium salts	9
GB1077366 (A)	Production of n:n'-disubstituted bipy...	10
GB1075323 (A)	Manufacture of bipyridyl derivatives	11
GB1073082 (A)	Tetrahydro-4:4'-bipyridyl derivatives...	12
GB1073824 (A)	Separation of a 4:4-bipyridylium salt...	13
GB1084868 (A)	Separation of bipyridylium and pyridi...	14
GB1073332 (A)	Quaternary salts of halogenated polymers	15
GB1095124 (A)	Bipiperidyl derivatives and processes...	16
GB1129511 (A)	Production of a pyridyl piperidine	17
GB1130551 (A)	Production of a pyridyl piperidine	18
GB1087052 (A)	Manufacture of 1,1'-alkylene-2,2'-	19
GB1108174 (A)	Bipyridylium compounds and herbicidal...	20
IL23305 (A)	PRODUCTION OF HERBICIDAL BIS-QUATERNA...	21
GB1078846 (A)	1,1'-alkylene-2,2'-bipyridylium halides	22
GB1082205 (A)	Manufacture of herbicidal materials c...	23
GB1043356 (A)	Purification of bipyridyls	24
GB1070504 (A)	Herbicidal compositions	25
GB969812 (A)	Catalytic process for the production ...	26

PATENT SPECIFICATION

(11) 1 268 191

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NO DRAWINGS

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 (72) Inventor ROY DENNIS BOWDEN



(54) PROCESS FOR THE MANUFACTURE OF BIPYRIDYLS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pyridine derivatives and their manufacture and particularly to a process for the manufacture of bipyridyls from substituted pyridines.

According to the present invention we provide a process for the manufacture of bipyridyls other than 3,3'-bipyridyls which comprises reacting the corresponding substituted pyridine with ammonia in the vapour phase, the substituted pyridine being a 2-(pyridyl)-tetrahydropyran or -tetrahydrothiopyran, a 4-(pyridyl)-tetrahydropyran or -tetrahydrothiopyran or a substituted pyridine wherein the substituent is a group of the structural formula $-C(R)(R_1)(R_2)$ wherein R represents a hydrogen atom, a halogen atom, a hydroxy group, an alkoxy group or an amino group, and R_1 and R_2 each represents a group of the general formula $-CH_n(XR_3)_{2-n} \cdot CH_m(XR_4)_{3-m}$ wherein X represents an atom of oxygen or sulphur, n is 0, 1 or 2 and m is 1 or 2, and R_3 and R_4 each represents a hydrogen atom or an alkyl, alkenyl, aryl, alkaryl, aralkyl or cyclo-aliphatic group. In the pyridine derivatives (including the pyridyl tetrahydropyrans and tetrahydrothiopyrans), the substituent may be in the 2, 3 or 4 position in the pyridine nucleus.

The reaction is preferably carried out in the presence of molecular oxygen, for example oxygen gas.

The substituted pyridine starting material in the vapour phase is heated with ammonia advantageously at a temperature in excess of 250° C., preferably 350—450° C., for example about 380° C., usually in the presence of catalyst. Suitable catalysts include alumina, silica, silica-alumina, magnesia, chromia and mixtures thereof; these catalysts may contain platinum and/or palladium (as the metal or its oxide) in finely-divided form. Particularly suitable catalysts are the dehydrogenation catalysts, e.g. nickel, cobalt, copper, chromium and copper chromite. Preferably the reaction mixture contains molecular oxygen as, for example, oxygen gas which can be conveniently added in the form of air, although any molecular oxygen containing gas may be used. If the reaction is carried out in the absence of oxygen, the reaction product subsequently may be oxidised to the bipyridyl with molecular oxygen.

The starting material can be vaporised simply by heating it to the required temperature and a particularly suitable technique is to drop the material in a stream of droplets onto a hot surface, for example onto a vaporiser or onto the catalyst for the reaction with ammonia. The material can be conveniently vaporised in a vaporiser prior to contact with the catalyst. Some of the starting materials are, however, tacky, viscous liquids or solids at ordinary temperatures and these are conveniently dissolved in a suitable solvent prior to vaporisation. Examples of suitable solvents for

1

PROCESS FOR PRODUCING 4,4'-BIPYRIDYL FROM 4,4' - BI(4H)PYRAN OR 4,4' - BIPYRYLENE BY AMMOXIDATION

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No Drawing. Filed Mar. 3, 1969, Ser. No. 803,983
Claims priority, application Great Britain, Mar. 15, 1968, 12,643/68

U.S. Cl. 260—296 D Int. Cl. C07d 31/42 11 Claims

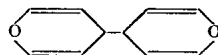
ABSTRACT OF THE DISCLOSURE

4,4'-bi(4H)pyrans and 4,4'-bipyrylenes are disclosed. These products are made by reducing the corresponding pyrylium salt whereby two molecules of the salt are coupled together to form the bi-(4H)-pyran and the bi-pyrylene. The 4,4'-bi(4H)-pyran or 4,4'-bipyrylene may be treated in the liquid phase with ammonium ions or ammonia in the presence of molecular oxygen to produce a 4,4'-bi-pyridyl.

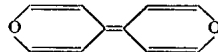
This invention relates to the production of novel oxygen-containing heterocyclic compounds and more particularly to bipyrans and bipyrylenes and their production, and to the production of bipyridyls.

According to the present invention we provide, as new compounds, 4,4'-bi(4H)-pyrans and 4,4'-bipyrylenes.

4,4'-bi(4H)-pyran has the structural formula:



and 4,4'-bipyrylene has the structural formula:



and included within the scope of the invention are compounds having these basic formulae but containing one or more substituents for example alkyl groups in the heterocyclic nuclei.

According to the invention we also provide a process for the production of a 4,4'-bi(4H)-pyran and a 4,4'-bipyrylene which comprises reducing the corresponding pyrylium salt whereby two molecules of the salt are coupled together to form the bi(4H)-pyran and the bipyrylene.

The reduction may be carried out by chemical or electrolytic means. Suitable chemical reducing agents are those having a redox potential more negative than -0.78 volt in an aqueous system as compared with the saturated calomel electrode and include organic and inorganic reducing agents. Examples of suitable inorganic reducing agents are active metals such as zinc, or zinc amalgam.

Electrolytic reduction may be achieved at electrode potentials in an aqueous system more negative than -0.78 volt with respect to the saturated calomel electrode and using apparatus conventionally used in electrolytic reduction processes. In particular the reduction may be carried out at the cathode of an electrolytic cell, the cathode being of mercury or another metal of high hydrogen overpotential, for example copper or lead. The electrolyte is an aqueous medium, preferably neutral or acidic, containing the pyrylium salt to be reduced.

The reduction, either by chemical or electrolytic means, may conveniently be carried out in an aqueous medium. The solution preferably has a pH of less than 7 since pyrylium salts tend to hydrolyse in aqueous alkaline solution. Also, the reduction is preferably carried out in the presence of an organic solvent for the pyrylium salt

2

starting material and for the bipyran product, for example acetone or a water-immiscible organic solvent, for example diethyl ether and hydrocarbons for example toluene and benzene, and alcohols particularly those of high molecular weight.

The reduction may be carried out over a wide range of temperatures, for example from -30° C. to +30° C. although higher or lower temperatures than these may be used if desired.

The product of the reduction comprises a mixture of a 4,4'-bi(4H)-pyran and a 4,4'-bipyrylene together with some by-products which are usually in the form of polymeric material. The product may be separated into its component compounds by conventional means, for example by preparative gas/liquid chromatography. The bipyrans and bipyrylenes of our invention may be converted to 4,4'-bipyridyls. A further feature of the invention, therefore, is the provision of a process for the production of a 4,4'-bipyridyl by treatment of a 4,4'-bi(4H)-pyran or 4,4'-bipyrylene in the liquid phase with ammonium ions or ammonia in the presence of molecular oxygen.

Ammonium ions may be introduced into the reaction mixture as such or they may be generated in situ. It is preferred to introduce ammonium ions in the form of an ammonium salt, and suitable ammonium salts include the salts of aliphatic acids, for example ammonium acetate, and the salts of mineral acids, for example ammonium sulphate, ammonium nitrate and ammonium chloride. Alternatively, gaseous ammonia or a solution of ammonia may be introduced into the reaction mixture. Amides hydrolysable to form ammonium ions, for example formamide or urea, may also be employed.

It is preferred to carry out the conversion of the bipyran and bipyrylene to 4,4'-bipyridyl under conditions such that the ammonia is present predominantly as an ammonium salt rather than as free ammonia and for this reason the pH range of from 1 to 7 is especially preferred.

It is preferred to use at least two moles of ammonium ion or ammonia per mole of the bipyran and/or the bipyrylene. The concentration of ammonium ions in the reaction mixture is preferably at least 0.01 molar, for example in the range 0.01 to 2.0 molar.

The reaction medium for the conversion of the bipyran and/or bipyrylene to 4,4'-bipyridyl may comprise water and/or an organic solvent; mixtures of water with one or more organic solvents are especially suitable. A wide range of organic solvents may be used but it is preferred to use an alkanolic acid containing up to 6 carbon atoms in the alkyl group, for example acetic acid or propionic acid. It is especially preferred to use aqueous acetic acid solution containing, for example, from 2% to 50% by weight of acetic acid.

When an ammonium salt is employed in the conversion, the desired acidity of the reaction mixture may be derived from the ammonium salt but additional acid may be provided if necessary. If a free acid is added, this can be conveniently the acid corresponding to the acid radical of the ammonium salt employed. Thus in a preferred embodiment of the invention, aqueous acetic acid is used as the reaction medium and ammonium acetate is used as the source of ammonium ions.

The conversion may be carried out over a wide range of temperature and pressure, depending partly upon the particular reactants and reaction medium used. In general, it is preferred to use temperatures in the range from 15° C. to 150° C., especially in the range from 80° C. to 130° C.

Preferably, the conversion is carried out at a pressure in the range from 1 to 30 atmospheres, for example in the range from 1 to 20 atmospheres; higher pressure, for example up to 50 atmospheres, may however be employed.

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3,598,826
PRODUCTION OF 1,1'-ETHYLENE-1,1',2,2'-
TETRAHYDRO-2,2'-BIPYRIDYL

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England, assignors to Imperial Chemical Industries
Limited, London, England

No Drawing. Filed Sept. 26, 1968, Ser. No. 763,002
Claims priority, application Great Britain, Oct. 10, 1967,
45,542/67

Int. Cl. C07d 51/64

U.S. Cl. 260—268

2 Claims

ABSTRACT OF THE DISCLOSURE

1,1'-ethylene-1,1',2,2'-tetrahydro-2,2'-bipyridyls, useful as intermediates for the manufacture of herbicides, as prepared by the reduction of ethylene-bis-pyridinium salts.

This invention relates to 1,1'-ethylene-1,1',2,2'-tetrahydro-2,2'-bipyridyls and to processes for their manufacture.

According to our invention we provide 1,1'-ethylene-1,1',2,2'-tetrahydro-2,2'-bipyridyls and in particular 1,1'-ethylene-1,1',2,2'-tetrahydro-2,2'-bipyridyl itself.

The pyridine rings in the tetrahydrobipyridyl may be unsubstituted or may carry inert substituents, for example alkyl groups, and in particular methyl or ethyl groups on one or more of the 3,3',4,4',5,5',6 or 6' positions. The two carbon atoms of the ethylene group may each carry hydrogen atoms and/or inert substituents, for example alkyl groups and in particular methyl or ethyl groups.

According to our invention we also provide a process for the manufacture of 1,1'-ethylene-1,1',2,2'-tetrahydro-2,2'-bipyridyl which comprises reducing a corresponding ethylene-bis-pyridinium salt.

The ethylene-bis-pyridinium salt may be in particular a salt of a strong acid, for example a halide (especially a chloride or a bromide), a sulphate, a chlorate or a perchlorate. Ethylene-bis-pyridinium salts may be made in conventional manner for example by interacting an ethylene dihalide and in particular an ethylene dibromide with a pyridine.

The reduction is preferably carried out in an aqueous medium and advantageously in the presence of an organic solvent, which is preferably one which is immiscible with the aqueous medium and is not affected itself by the reductive process and may be in particular a hydrocarbon or an ether, for example benzene, toluene, xylene, trimethyl benzenes, hexane, cyclohexane, iso-octane, n-decane, petroleum ether or other petroleum fractions, diethyl ether, di-n-propyl ether, dibutyl Carbitol, or mixtures thereof. It is also possible to use other water-immiscible organic solvents even if they have some possibility of reacting (for example by being reduced), provided that such side reaction does not either interfere with the course of the desired reduction of the pyridinium salt or produce by-products which interfere with the isolation or recovery of the desired tetrahydrobipyridyl product. Mixtures of solvents may also be used if desired. The main consideration for choice is usually the boiling point of the solvent, which should be convenient for the operation to be carried out. It is advantageous for the solvent to have a specific gravity less than 1, as this aids separation of the organic solvent phase (containing the product) from the aqueous phase after reaction.

The reduction may be carried out by means of a suitable chemical reducing agent, for example an active metal and in particular an alkali metal, magnesium, calcium or aluminium. We have found it convenient to carry out the reduction by means of an alkali metal amalgam, particularly sodium amalgam, and for this purpose it is more

convenient to use an amalgam which is liquid. The reaction may be carried out by agitating the mixture of aqueous pyridinium salt solution, amalgam, and the organic solvent until reaction has proceeded to the desired degree after which the mixture can be allowed to settle, and the organic solvent phase containing the tetrahydrobipyridyl product can be separated. The mercury (i.e. spent amalgam) phase can also be recovered for re-use.

Alternatively the reduction can be carried out electrolytically. High yields and current efficiencies may be obtained by using neutral or alkaline aqueous solutions of the ethylene-bis-pyridinium salt as electrolyte and maintaining the cathode potential within ± 0.2 volt of the polarographic half-wave potential for the reduction of the particular ethylene-bis-pyridinium salt used. In the case of the reduction of unsubstituted ethylene-bis-pyridinium salts it is preferred to maintain the cathode potential in the range -1.06 ± 0.2 volt with reference to a saturated calomel electrode. Complete conversion of the ethylene-bis-pyridinium salt to the tetrahydrobipyridyl derivative can be achieved, without reduction in the current efficiency, if the current is reduced during the course of the electrolysis at a rate such as to maintain the potential in the desired range. The addition of a salt which has a high conductance in solution, for example sodium chloride, to the electrolyte, improves the conductivity of the electrolyte and decreases the specific electrical energy consumption (kilowatt-hours per unit of tetrahydrobipyridyl produced) for the electrolysis.

The cathode material may be conveniently mercury, though other metals, preferably of high hydrogen overpotential (for example copper or lead) may also be used.

The concentration of the ethylene-bis-pyridinium salt in the aqueous solutions used in these reduction procedures may be any convenient concentration up to saturation level, though we prefer not to use very dilute solutions. When additional salts are added to the solution, as for example to improve the conductivity for the electrolytic reduction, allowance should be made for the fact that a high concentration of ethylene-bis-pyridinium salt may reduce the solubility of the salts being added. Accordingly, the optimum concentrations of both ethylene-bis-pyridinium salt and additive salts are inter-related and we prefer that the concentration of salts other than the ethylene-bis-pyridinium salt are kept below 5 molar concentration.

The reduction may be carried out at a variety of temperatures, though it is preferred to use a temperature at which the tetrahydrobipyridyl product (which may in some circumstances be an unstable compound) is not decomposed to any troublesome extent. In general, a temperature in the range approximately 20° to 30° C. is very convenient. It is also desirable, because of the possible instability of the product, to carry out the reduction under an inert atmosphere, for example of nitrogen or argon.

The compounds of this invention are useful as intermediates, for example for the production of the corresponding bipiperidyl and are especially useful for conversion by oxidation into the corresponding N,N'-ethylene-2,2'-bipyridylium salts, of value as herbicides.

The invention is illustrated but not limited by the following examples in which the parts and percentages are by weight. The reaction described in these examples were carried out under high purity nitrogen and nitrogen was passed through the solvents and solutions to remove air before the solvents and solutions were used.

EXAMPLE 1

Ethylene-bis-pyridinium bromide (2.208 grams dissolved in 10 ml. of water) was added, drop-wise over a period of about 30 minutes to a stirred mixture of sodium amalgam (10 ml. containing about 0.45 percent of so-

PATENT SPECIFICATION

NO DRAWINGS

Inventors: JOHN EDWARD DOWNES and JANET ELISABETH JAMESON

1,135,682



1,135,682

Date of filing Complete Specification (under Section 3 (3) of the Patents Act 1949): 6 Oct., 1967.

Two Applications Dated: 7 Nov., 1966. Nos. 49800/66 and 49801/66.

Complete Specification Published: 4 Dec., 1968.

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Index at acceptance:—C2 C(B4A2, B4K)

Int. Cl.:—C 07 d 31/22

COMPLETE SPECIFICATION

Process for Preparing Bipyridylum Compounds

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of alkyl quaternary salts of 4,4'-bipyridyls.

Previously proposed methods for the production of N-alkyl-4,4'-bipyridylum diquaternary salts require the use of alkyl halides or alkyl sulphates as quaternising agents. These quaternising agents, however, suffer from various disadvantages. For example, dimethylsulphate is a toxic substance which is dangerous to handle, while methyl chloride requires the use of pressures above atmospheric pressure to obtain a satisfactory yield of product. We have now discovered that N - alkyl - 4,4' - dipyridylum diquaternary salts can be prepared by an alternative reaction process.

According to the present invention, we provide a process for the production of N-alkyl diquaternary salts of 4,4'-bipyridyls which comprises heating a 4,4'-bipyridyl for a period of at least three minutes with an aliphatic carboxylic acid containing 2 to 5 carbon atoms substituted in the alpha position with a radical capable of conversion into a stable negative ion and recovering an N-alkyl-4,4'-diquaternary dipyridylum salt.

The process may if desired be carried out in the presence of an inert diluent.

Suitable 4,4'-bipyridyls for use in the process include 4,4'-bipyridyls substituted in one or both rings with one or more alkyl groups, especially one or more alkyl groups having from one to four carbon atoms. Examples are

2,2'-dimethyl-4,4'-bipyridyl and 2,6-dimethyl - 4,4' - bipyridyl. 4,4' - Bipyridyl is particularly suitable.

The process may conveniently be carried out by heating an admixture of the reactants to a temperature of from 80° to 150°C. A particularly suitable temperature is 120°C. The reaction mixture is maintained at this temperature for at least three minutes and conveniently about ten minutes. While generally no practical advantage is gained from very extensive reaction times e.g. longer than two hours, there is no actual upper limit to the length of time which may be taken if desired. Recovery of the product from the reaction mixture may be carried out by any of a variety of known techniques, e.g. solvent recrystallisation.

The reaction may also be carried out by heating the reactants in the presence of an inert diluent, preferably a solvent having a boiling point of at least 100°C. The temperature of reaction when using a diluent is generally between 80° and 250°C. and preferably 150° to 200°C. The time necessary for reaction varies according to the temperature and the reactants from a few minutes upward; generally one or two hours are sufficient.

In general, any inert organic diluent or water can be used, but particularly preferred diluents are polar, for example ethoxyethanol and N,N'-dimethylformamide. The solvent can be used alone or together with a wetting agent, or a substance may be used which possesses wetting properties and at the same time is capable of acting as a diluent, for example a condensate of nonyl phenol and ethylene oxide sold under the Trade Mark "Lissapol".

Another particularly useful class of substances capable of acting both as a wetting

[Price

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3,478,042

PRODUCTION OF N:N-DISUBSTITUTED TETRAHYDRO-4:4'-BIPYRIDYL WITH THE USE OF A WATER IMMISCIBLE SOLVENT IN A REDUCTION PROCESS

John Edward Colchester and John Hubert Entwisle, Runcorn, England, assignors to Imperial Chemical Industries Limited, Millbank, London, England, a corporation of Great Britain

No Drawing. Filed Apr. 11, 1966, Ser. No. 541,505

Int. Cl. C07d 31/40

U.S. Cl. 260—296

9 Claims

ABSTRACT OF THE DISCLOSURE

There is provided a process for the manufacture of a N:N'-disubstituted tetrahydro-4:4'-bipyridyl which comprises reducing the corresponding N-substituted pyridinium salt in an aqueous medium. The improvement resides in carrying out the reduction in the presence of an immiscible organic solvent for the tetrahydrobipyridyl product. With the use of such a solvent the product is removed from the reduction zone and increases the yield of the reduction. Examples of such solvents are diethyl ether, tetrahydrofuran and benzene.

This invention relates to a process for the manufacture of organic bases and more particularly for the manufacture of N:N'-disubstituted tetrahydro-4:4'-bipyridyls.

It is known that aqueous solutions of N-methylpyridinium salts and some analogous compounds can be reduced either electrolytically or with sodium amalgam to form the corresponding N:N'-disubstituted tetrahydro-4:4'-bipyridyls. The product of reduction may be either an oil or a solid. Particularly when the product is an oil, we find that reaction can be slow or incomplete, and that this effect is apparently due to the accumulation of the product in the zone of reduction. Also, this oily product tends to cling to metal (e.g. amalgam) surfaces, and accumulation of this can cause polarisation in the case of an electrolytic process and in the case of an amalgam reduction can promote the formation of emulsions of mercury in the reaction mixture. When the reduction product is a solid, losses of mercury tend to arise in the amalgam reductions due to entrainment in the product and these losses may be considerable.

We have now found that these difficulties can be overcome by carrying out the reduction in the presence of an organic solvent for the tetrahydro bipyridyl product, which dissolves it and removes it from the reduction zone.

Thus according to our invention we provide a process for the manufacture of an N:N'-disubstituted tetrahydro-4:4'-bipyridyl which comprises reducing the corresponding N-substituted pyridinium salt in aqueous medium in the presence of an immiscible liquid organic solvent for the tetrahydro-bipyridyl product.

The organic solvent for the purposes of our invention is preferably one which is immiscible with the aqueous medium and is not affected itself by the reductive process and may be in particular a hydrocarbon or an ether, for example benzene, toluene, xylene, trimethyl benzenes, hexane, iso-octane, n-decane, petroleum ether or other petroleum fractions, diethyl ether, di-n-propyl ether, tetrahydrofuran, dibutyl carbitol, or mixtures thereof. It is also possible to use other water-immiscible organic solvents, even if they have some possibility of reacting (for example by being reduced), provided that such side reaction does not either interfere with the course of the desired reduction of the pyridinium salt or produce by-products which interfere with the isolation or recovery of

2

the desired tetrahydrobipyridyl product. Mixtures of solvents may also be used if desired. The main consideration for choice is usually the boiling point of the solvent, which should be convenient for the operations to be carried out. It is advantageous for the solvent to have a specific gravity less than 1, as this aids separation of the organic solvent phase (containing the product) from the aqueous phase after reaction.

The process of our invention is especially applicable to the case in which the product is an oil, as is the case when the starting material is an N-alkyl-pyridinium salt, for example N-methyl- and N-ethyl-pyridinium chlorides. The process is also applicable to the use, as starting material, of a benzyl pyridinium salt, or a pyridinium salt having as N-substituent a carbamido alkyl substituent, particularly one of the form $-R_1-CO-NR_2R_3$ wherein R_1 is a hydrocarbon radical (especially the methylene radical) and R_2 and R_3 are hydrocarbon or substituted hydrocarbon radicals, and wherein R_2 and R_3 may, together with the attached nitrogen atom, make up a heterocyclic ring. Examples of these starting materials include the products made by reaction of pyridine with N:N'-disubstituted chloracetamides, for example N:N'-diethyl chloracetamide, N-(chloroacetyl)-piperidine and N-(chloroacetyl)-3,5-dimethyl morpholine. The salt is conveniently a halide salt, though others may be used if desired.

The reduction may be carried out conveniently by means of an alkali metal amalgam, particularly sodium amalgam. For this purpose it is more convenient to use an amalgam which is liquid. The reaction may be carried out by agitating the mixture of aqueous pyridinium salt solution, amalgam, and the organic solvent until reaction has proceeded to the desired degree, after which the mixture can be allowed to settle, and the organic solvent phase containing the tetrahydrobipyridyl product can be separated. The mercury (i.e. spent amalgam) phase can also be recovered for re-use.

Alternatively the reduction can be carried out electrolytically. High yields and current efficiencies can be obtained by using neutral or alkaline aqueous solutions of the N-substituted pyridinium salt as electrolyte and maintaining the cathode potential within ± 0.2 volt of the polarographic half-wave potential for the reduction of particular pyridinium salt used. In the case of the reduction of N-methyl-pyridinium salts it is preferred to maintain the cathode potential in the range -1.45 ± 0.2 volt with reference to a saturated calomel electrode. Complete conversion of the pyridinium salt to the tetrahydro bipyridyl derivative can be achieved, without reduction in the current efficiency, if the current is reduced during the course of the electrolysis at a rate such as to maintain the potential in the desired range. The addition of a salt which has a high conductance in solution, for example sodium chloride, to the electrolyte improves the conductivity of the electrolyte and decreases the specific electrical energy consumption (kilowatt-hours per unit of tetrahydrobipyridyl produced) for the electrolysis.

The cathode material may be conveniently mercury, though other metals, preferably of high hydrogen over potential (for example copper or lead) may also be used.

The concentration of the pyridinium salt in the aqueous solutions used in these reduction procedures may be any convenient concentration up to saturation level, though we prefer not to use very dilute solutions. When additional salts are added to the solution, as for example to improve the conductivity for the electrolytic reduction, allowance should be made for the fact that high concentrations of pyridinium salt may reduce the solubility of the salts being added. Accordingly, the optimum concentrations of both pyridinium salt and additive salts are



PATENT SPECIFICATION

NO DRAWINGS

Inventor: ANTHONY EDWARD SMITH

Date of filing Complete Specification: 9 Jan., 1967.

Application Date: 21 Jan., 1966.

Complete Specification Published: 10 July, 1968.

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1,119,544

No. 2837/66.

Index at acceptance:—C2 C(B4A2, B4K); C4 P(Q4A1, Q4A2, Q4A3, Q4A7)

Int. Cl.:—C 07 d 31/22

COMPLETE SPECIFICATION

Production of N:N'-Disubstituted Bipyridylium Salts

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of N:N' - disubstituted - 4:4' - bipyridylium salts.

In our copending Application Nos. 14720/64 and 36729/64 (Specification No. 1,073,081) there is described a process for the production of N:N' - disubstituted - 4:4' - bipyridylium salts by the oxidation of an N:N' - disubstituted - tetrahydro - 4:4' - bipyridyl using an organic oxidising agent which is a hydrogen acceptor and which has a redox potential more positive than -1.48 volts with respect to the standard calomel electrode.

We have now found that N:N' - disubstituted - tetrahydro - 4:4' - bipyridyls may advantageously be converted to the corresponding bipyridylium salts by the use of particular oxidising agents which can be regenerated by oxygen.

Thus according to our invention we provide a process for the production of an N:N' - disubstituted - 4:4' - bipyridylium salt which comprises treating an N:N' - disubstituted - tetrahydro - 4:4' - bipyridyl with a substituted 9,10 - anthraquinone, the substituted 9,10 - anthraquinone being such that the corresponding 9,10 - anthraquinol can be oxidised to the substituted 9,10 - anthraquinone by oxygen and also being such that it is a hydrogen acceptor and has a redox potential more positive than -1.48 volts with respect to the standard calomel electrode.

The substituted 9,10 - anthraquinone preferably has no substituent on its alpha-carbon atoms as we have found that such substituents tend to slow the rate of reaction, possibly by steric hindrance of the 9 and/or

10 positions. If, however, alpha-substituents are present they should preferably be few and small if a high rate of reaction is required. We have found that a suitable group of substituted 9,10 - anthraquinones are those containing one or more electron-withdrawing substituents, for example halogen atoms and especially one or more chlorine atoms. Amongst this group of compounds we have found that 1 - chloro - 9,10 - anthraquinone, 1,5 - dichloro - 9,10 - anthraquinone, 1,8 - dichloro - 9,10 - anthraquinone and 2,6 - dichloro - 9,10 - anthraquinone and in particular 2 - chloro - 9,10 - anthraquinone, give satisfactory results.

The N:N' - disubstituted - tetrahydro - 4:4' - bipyridyl may be in particular the N:N' - dialkyl - tetrahydro - 4:4' bipyridyl or N:N' - dicarbamylalkyl - tetrahydro - 4:4' - bipyridyls more fully described in Belgian Patent No. 662,281.

The reaction may be carried out conveniently in solution in an inert solvent which will dissolve both the N:N' - disubstituted - tetrahydro - 4:4' - bipyridyl and the substituted 9,10 - anthraquinone. Substituted 9,10 - anthraquinones are not always readily soluble in organic solvents but we have in general found that suitable solvents can be selected from the following groups; ethers, for example diethyl ether, tetrahydrofuran, bis - (2 - methoxy ethyl) ether and the dibutyl ether of diethylene glycol; ketones, for example acetone and methyl ethyl ketone; hydrocarbons for example benzene and alkyl benzenes such as those known in commerce as "Aromasols"; inert halogenated hydrocarbons, particularly chlorinated hydrocarbons, for example methylene chloride; and mixtures of such solvents. When it is desired to carry out the reaction in solution the choice of a suitable substituted 9,10-anthraquinone may be influenced by the solubility of the available substituted 9,10-anthraquinones in the available solvent media.

The rate of reaction depends on the par-

PATENT SPECIFICATION

NO DRAWINGS

Inventors: KENNETH NEWSHAM JONES and ALLAN WILLIAM OLLEVEANT

1.136.823



1.136.823

Date of filing Complete Specification: 4 Jan., 1967.

Application Date: 14 Jan., 1966.

No. 1936/66.

Complete Specification Published: 18 Dec., 1968.

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Index at acceptance: —C1 AQ8B

Int. Cl.: —C 01 d 1/02

COMPLETE SPECIFICATION

Production of Alkali Metal Oxides

We IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of alkali metal super-oxides and more particularly to the production of sodium superoxide.

According to the invention we provide a process for the production of an alkali metal superoxide (other than that of lithium) which comprises oxidising an alkali metal/bipyridyl interaction product with an oxidising agent containing or capable of releasing available oxygen and which is inert towards the alkali metal superoxide. The alkali metal peroxide is usually produced in addition to the superoxide.

By a superoxide we mean an oxide of formula XO_2 or X_2O_4 where X stands for the alkali metal.

We prefer to carry out the process in two distinct steps, the first of which comprises the interaction of the alkali metal and the bipyridyl to form the interaction product and the second of which comprises the oxidation of the alkali metal-bipyridyl interaction product. However, an alternative method in which the oxidant is present in the interacting mixture of alkali metal and bipyridyl is also suitable.

The production of a alkali metal/bipyridyl interaction product is best carried out by interaction of the alkali metal and the bipyridyl in a solvent. The solvent may conveniently be liquid ammonia or may be a mixture of liquid ammonia and an inert diluent. Suitable inert diluents are those more fully described in, and more particularly those

specified in Claims 13 to 19 of, U.K. Patent Specification No. 1,030,154. The proportion of liquid ammonia in the solvent should be at least sufficient to dissolve the alkali metal. It is also preferred that the oxidation step be carried out in the presence of a solvent or diluent, which may conveniently be that used in the production of the interaction product.

The interaction of the alkali metal and the bipyridyl may be carried out simply by mixing a solution of the alkali metal with a solution of the bipyridyl. For example a solution of alkali metal in liquid ammonia may be mixed with a solution of bipyridyl in the inert diluent. The concentration of metal in the solvent before the solvent is mixed with the bipyridyl is conveniently in the range 2—10% by weight, and the solution of bipyridyl before it is mixed with the solution of alkali metal is suitably one which is saturated with bipyridyl. We prefer to carry out the interaction of the alkali metal and the bipyridyl at a temperature below -30°C .

We have found that 4:4'-bipyridyl is particularly suitable for use in our process but other bipyridyls, for example 2:2'-bipyridyl, may be used if desired.

When the interaction of the alkali metal and the bipyridyl is complete the resulting solution of metal-bipyridyl interaction product may be oxidised directly; alternatively the ammonia present in the solution may be allowed to evaporate and the resulting solution or suspension of the metal-bipyridyl interaction product in the inert diluent may then be oxidised.

In the case where 4:4'-bipyridyl is used the metal-bipyridyl interaction product is, we believe, of the type of the Ward radical which has the following structure:—

[Price 4s. 6d.]

PATENT SPECIFICATION

NO DRAWINGS

Inventors: JOHN EDWARD COLCHESTER and JOHN HUBERT ENTWISLE

1074.994



1074.994

Date of filing Complete Specification: May 17, 1966.

Application Date: May 28, 1965.

No. 22774/65.

Complete Specification Published: July 5, 1967.

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Index at acceptance:—C2 C(B4A2, B4K)

Int. Cl.:—C 07 d 31/24

COMPLETE SPECIFICATION

Production of Bipyridylum Salts

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of N:N'-disubstituted bipyridylum salts and particularly to the production of bis quaternary salts of 4:4'-bipyridyl.

It is known to interact sodium and pyridine at or above ambient temperature and then to react the resulting sodium pyridine interaction product with an alkyl halide, but hitherto this reaction has only produced a syrup which exhibited some of the properties of a tetrahydrobipyridyl but from which it was not possible to isolate N:N'-dialkyl tetrahydrobipyridyls. It is also known from our copending U.K. Specification No. 1,030,154 to form a metal pyridine interaction product for example a sodium pyridine interaction product by the action of a solution of a metal in an anhydrous liquid medium containing ammonia on a pyridine.

We have now found a convenient process for the production of bipyridylum salts from pyridines using a metal-pyridine interaction product made for example by the process described in our copending U.K. Specification No. 1,030,154.

Thus according to our invention we provide a process for the production of an N:N'-disubstituted bipyridylum salt which comprises interacting a pyridine with a solution of an alkali metal or alkali earth metal in a substantially anhydrous liquid medium containing ammonia to form a metal-pyridine interaction product, reacting the metal-pyridine interaction product with an organic compound containing

only one reactive halogen atom per molecule to form an N:N'-disubstituted 1:1':4:4'-tetrahydro-4:4'-bipyridyl, and thereafter converting the N:N'-disubstituted 1:1':4:4'-tetrahydro-4:4'-bipyridyl to a bipyridylum salt.

The metal solution may be made and interacted with the pyridine as is described in our copending U.K. Specification No. 1,030,154. In particular we prefer to use a solution of an alkali metal, for example sodium or potassium in a substantially anhydrous solvent containing liquid ammonia and optionally an inert organic diluent such as an ether. Suitable ethers for this purpose include in particular polyethers in which two ether oxygen atoms are separated by a chain of two carbon atoms. It is preferred that the ether should contain in its structure at least one terminal methoxy group. Thus there may be used for example, ethers of tetrahydrofurfuryl alcohol (for example the methyl ether) and di-ethers of ethylene glycol, and especially 1:2-dimethoxyethane, bis-(2-methoxyethyl) ether and 1:2-bis-(2-methoxyethyl) ether is most suitable. Alternatively there may be used a solution of lithium or calcium in a similar solvent to that described above for sodium and potassium. The metal-pyridine interaction product produced by the use of sodium in our process is we believe an N:N'-disodium 1:1':4:4'-tetrahydro-4:4'-bipyridyl.

The pyridine used in the production of the metal-pyridine interaction product may be pyridine itself, or may be a pyridine carrying substituents which do not interfere with the reaction, for example pyridine carrying alkyl substituents in the 2,3,5 or 6 positions.

The organic halogen compound preferably contains only one halogen atom per molecule, the halogen atom preferably being chlorine, bromine or iodine. Use of compounds contain-

PATENT SPECIFICATION

NO DRAWINGS

1077.366

1077.366



Inventors: JOHN EDWARD COLCHESTER and JOHN HUBERT ENTWISE

Date of filing Complete Specification: May 13, 1966.

Application Date: May 28, 1965.

No. 22773/65.

Complete Specification Published: July 26, 1967.

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Index at acceptance:—C2 C(B4A2, B4K)

Int. Cl.—C 07 d 31/22

COMPLETE SPECIFICATION

Production of N:N'-Disubstituted Bipyridylium Salts

ERRATUM

SPECIFICATION No. 1,077,366

Page 1, Heading, *Inventors:* for "JOHN HUBERT ENTWISE" read "JOHN HUBERT ENTWISLE"

THE PATENT OFFICE
5th February 1968

15 compounds are usually made by a quaternisation reaction from 4:4'-bipyridyl. It is also known that N:N'-dibenzyl tetrahydrobipyridyl can be oxidised to an N:N'-dibenzyl bipyridylium salt by the action of iodine, but this process gives only poor yields of the bipyridylium salt, and much of the starting material is converted into benzyl pyridinium salts by fission of the bond connecting the two pyridine rings.

25 In our copending U.K. Applications Nos. 14720/64 and 36729/64 (Serial No. 1,073,081) we have described processes whereby N:N'-disubstituted - 1:1':4:4' - tetrahydro - 4:4'-bipyridyls may be oxidised to N:N' - disubstituted - 4:4' - bipyridylium salts by organic oxidants particularly quinones. We have now found that the N:N' - disubstituted - 1:1':4:4' - tetrahydro - 4:4' - bipyridyls may be converted in good yield into N:N' - disubstituted - 4:4' - bipyridylium salts by the action of compounds containing a labile halogen atom.

40 Thus according to our invention we provide a process for the conversion of N:N'-disubstituted - 1:1':4:4' - tetrahydro - 4:4'-bipyridyls to N:N' - disubstituted - 4:4'-bipyridylium halides which comprises treating the tetrahydrobipyridyl with one or more

for example alkyl groups, on the carbon atoms of the pyridine nuclei.

The carbon compound containing a labile halogen atom may be any such compound which is capable of removing hydrogen from the tetrahydrobipyridyl, for example a compound containing a carbon-to-halogen bond of dissociation energy less than about 70 k cal/mole. Such carbon compounds include those in which the halogen is attached to a carbon atom which is attached to an electron withdrawing group for example a —CHal₃ (where Hal = Cl, Br or I), —CO, —F, —Br or —Cl group. We have found that it is convenient to use liquid or solid carbon compounds and particularly liquid or solid compounds containing less than 4 carbon atoms per molecule. Bromine and iodine atoms tend to be more labile than chlorine atoms when attached to carbon and compounds containing bromine and iodine will therefore tend to be more effective than those containing chlorine only. However compounds containing bromine and iodine are relatively expensive and it is therefore economically desirable to use the cheaper compounds containing chlorine. We also prefer to use highly halogenated compounds and in particular fully halogenated compounds such as carbon tetra-

[Pri.]

PATENT SPECIFICATION

1,075,323

NO DRAWINGS.

*Inventors:—*JOHN EDWARD COLCHESTER and JOHN HUBERT ENTWISLE.

Date of filing Complete Specification: March 29, 1966.

Application Date: April 7, 1965. No. 14776/65.

Complete Specification Published: July 12, 1967.

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1,075,323



Index at Acceptance:—C2 CB4A2; C7 B2C.

Int. Cl.:—C 07 d 31/24.

COMPLETE SPECIFICATION.

Manufacture of Bipyridyl Derivatives.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the manufacture of organic bases and more particularly for the manufacture of N:N¹-disubstituted tetrahydro-4:4¹-bipyridyls.

It is known that aqueous solutions of N-methylpyridinium salts and some analogous compounds can be reduced either electrolytically or with sodium amalgam to form the corresponding N:N¹-disubstituted tetrahydro-4:4¹-bipyridyls. The product of reduction may be either an oil or a solid. Particularly when the product is an oil, we find that reaction can be slow or incomplete, and that this effect is apparently due to the accumulation of the product in the zone of reduction. Also, this oily product tends to cling to metal (e.g. amalgam) surfaces, and accumulation of this can cause polarisation in the case of an electrolytic process and in the case of an amalgam reduction can promote the formation of emulsions of mercury in the reaction mixture. When the reduction product is a solid, losses of mercury tend to arise in the amalgam reductions due to entrainment in the product and these losses may be considerable.

We have now found these difficulties can be overcome by carrying out the reduction in the presence of an organic solvent for the tetrahydro-bipyridyl product, which dissolves it and removes it from the reduction zone.

Thus according to our invention we provide

a process for the manufacture of an N:N¹-disubstituted tetrahydro-4:4¹-bipyridyl which comprises reducing the corresponding N-substituted pyridinium salt in aqueous medium in the presence of a water-immiscible liquid organic solvent for the tetrahydro-bipyridyl product.

The organic solvent for the purposes of our invention is preferably one which is immiscible with the aqueous medium and is not affected itself by the reductive process and may be in particular a hydrocarbon or an ether, for example benzene, toluene, xylene, trimethyl benzenes, hexane, isooctane, n-decane, petroleum ether or other petroleum fractions, diethyl ether, di-n-propyl ether, tetrahydrofuran, dibutyl carbitol, or mixtures thereof. It is also possible to use other water-immiscible organic solvents, even if they have some possibility of reacting (for example by being reduced), provided that such side reaction does not either interfere with the course of the desired reduction of the pyridinium salt or produce by-products which interfere with the isolation or recovery of the desired tetrahydrobipyridyl product. Mixtures of solvents may also be used if desired. The main consideration for choice is usually the boiling point of the solvent, which should be convenient for the operations to be carried out. It is advantageous for the solvent to have a specific gravity less than 1, as this aids separation of the organic solvent phase (containing the product) from the aqueous phase after reaction.

The process of our invention is especially applicable to the case in which the product is an oil, as is the case when the starting material is an N-alkyl-pyridinium salt, for example N-methyl- and N-ethyl-

1.073.082



PATENT SPECIFICATION

NO DRAWINGS

1.073.082

Inventors: JOHN EDWARD COLCHESTER and
JOHN HUBERT ENTWISLE

Date of filing Complete Specification: March 29, 1966.

Application Date April 7, 1965.

No. 14775/65.

Complete Specification Published: June 21, 1967.

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Index at acceptance:—C2 C(2B53D1, 2B53G, 3A14B3D, 3A14B8D); C7 B2C

Int. Cl.:—C 07 d 29/40

COMPLETE SPECIFICATION

Tetrahydro-4:4'-Bipyridyl Derivatives and the preparation thereof

PATENTS ACT, 1949

SPECIFICATION NO. 1,073,082

The following corrections were allowed under Section 76 on 7th September, 1967

Page 2, line 31, for " $\text{R} - \text{CONR} \text{ R}$ " read " $\text{R} - \text{CONR} \text{ R}$ "
 $\begin{matrix} 1 & 1 & 2 \end{matrix} \quad \begin{matrix} 1 & 2 & 3 \end{matrix}$

THE PATENT OFFICE,
1st November 1967

D 93227/23

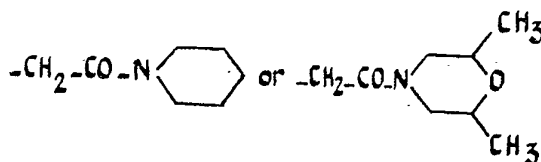
fication No. 999,585.

According to our invention we also provide a process for the production of tetrahydro - 4:4' - bipyridyls having as N-substituent on each nitrogen atom a group of the form $-\text{R}_1-\text{CO}-\text{NR}_2\text{R}_3$ wherein R_1 is a hydrocarbon radical (particularly the methylene group $-\text{CH}_2-$) and R_2 and R_3 are hydrocarbon or substituted hydrocarbon radicals, or wherein R_2 and R_3 , together with the nitrogen atom to which they are attached, make up a heterocyclic ring (for example a piperidine or a morpholine ring) which comprises reducing a quaternary pyridinium salt having the corresponding group $-\text{R}_1-\text{CO}-\text{NR}_2\text{R}_3$ as N-substituent.

The reduction which involves a reductive coupling of two molecules of the quaternary pyridinium salt may be carried out electrolytically at the cathode of a cell having an aqueous alkaline electrolyte, and using a cathode made of mercury, lead, or another metal of high hydrogen overpotential.

Alternatively the reduction may be carried out using an alkali metal amalgam, particularly sodium amalgam. We prefer to carry out the reduction at a temperature in the range 0 to 100°C.

The invention may be applied to produce tetrahydro - 4:4' - bipyridyls having a wide variety of suitably substituted carbamoylalkyl N-substituents, but there may be mentioned in particular the tetrahydro-4:4'-bipyridyl derivatives in which the N-substituents are for example $-\text{CH}_2-\text{CO}-\text{N}(\text{C}_2\text{H}_5)_2$, $-\text{CH}_2-\text{CO}-\text{N}[\text{CH}(\text{CH}_3)_2]_2$,



PATENT SPECIFICATION

NO DRAWINGS

Inventors: JOHN EDWARD COLCHESTER, JOHN HUBERT ENTWISLE, and
MAURICE BERKELEY GREEN

1,073,824



1,073,824

Date of filing Complete Specification: March 29, 1966.

Application Date: April 6, 1965.

No. 14577/65.

Complete Specification Published: June 28, 1967.

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Index at acceptance:—C2 C(B4A2, B4M)

Int. Cl.:—C 07 d 31/16

COMPLETE SPECIFICATION

Separation of a 4:4'-bipyridylum Salt from a Mixture Containing it

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a separation process useful in the production of herbicidal materials.

In our U.K. Application No. (Serial No. 1,073,081) 36729/64 there is described a process for the production of bis-quaternary salts of 4:4'-bipyridyl, which are useful as herbicidal materials, from an N:N'-dialkyl-tetrahydro-4:4'-bipyridyl, a quinone and an acid. This process produces small proportions of an N-alkyl pyridinium salt as a by-product. Other oxidising agents may be used in the place of the quinone but usually the reaction is then predominantly that of forming the N-methyl-pyridinium salt with relatively little of the bis-quaternary salt. In such processes it is very desirable to have not only a process for recovering the bis-quaternary salt (which is the commercially valuable material), but also a process which enables the N-alkyl pyridinium salt to be recovered. It is also very desirable to be able to recover the valuable bipyridylum salt from other mixtures or from dilute solutions containing it.

We have now found that 4:4'-bipyridylum salts form an insoluble derivative with amsonic acid, which can be used for the purpose of separation or recovery.

Thus according to the present invention we provide a process for the separation of a 4:4'-bipyridylum salt from mixtures or

solutions containing it which comprises treating a solution containing the said salt with amsonic acid, whereby the 4:4'-bipyridylum salt of amsonic acid is precipitated.

This process is especially applicable to bis-quaternary salts of 4:4'-bipyridyl and particularly to N:N'-dialkyl-4:4'-dipyridylum salts. The process is especially useful for separating such salts from admixture with an N-alkyl pyridinium salt.

Amsonic acid is a name commonly employed for 4:4'-diamino-stilbene-2:2'-disulphonic acid. As the acid itself is only sparingly soluble in water it is conveniently employed for the purpose of our invention in the form of an aqueous solution of one of its water-soluble salts, particularly an alkali metal salt or an ammonium salt.

The process is conveniently carried out at a pH in the range 7 to 12. At higher pH there is a tendency for the bipyridylum salt to decompose, and at lower pH there is a tendency for free amsonic acid to precipitate. The process is conveniently carried out at a temperature in the range 0 to 100°C.

The process of our invention may be conveniently carried out by taking the aqueous solution of mixed salts containing a 4:4'-bipyridylum salt, for example a solution such as is produced in the reaction described in our Specification (Serial No. 1,073,081) No. 36729/64, and adding to this an aqueous solution of amsonic acid, for example as its disodium salt, in sufficient quantity to provide a slight excess over that calculated to be equivalent to the 4:4'-dipyridylum salt present. For this purpose the quantity required is easily calculated from an analysis of the solution or material used as starting material. If it is inconvenient to analyse the

PATENT SPECIFICATION

NO DRAWINGS

Inventors: JOHN EDWARD COLCHESTER and JOHN HUBERT ENTWISLE

1084868



1084868

Date of filing Complete Specification: March 4, 1966.

Application Date: March 19, 1965.

No. 11771/65.

Complete Specification Published: Sept. 27, 1967.

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Index at acceptance:—C2 C(B4A2, B4J, B4K)

Int. Cl.:—C 07 d 31/16

COMPLETE SPECIFICATION

Separation of Bipyridylum and Pyridinium Salts

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a separation process useful in the production of herbicidal materials.

In our U.K. Application No. 36729/64 (Serial No. 1073081) there is described and claimed a process for the production of bis-quaternary salts of 4:4'-bipyridyl (which are useful as herbicidal materials) by the interaction of an N:N'-dialkyl-tetrahydro-4:4'-bipyridyl and a quinone and treatment of the interaction product with an acid. This process produces small proportions of an N-alkyl pyridinium salt as a by-product. Other oxidising agents may be used in the place of the quinones but the reaction is then predominantly that of forming the N-methyl-pyridinium salt with relatively little of the bis-quaternary salt. In such processes it is very desirable to have not only a process for recovering the bis-quaternary salt (which is the commercially valueable material), but also a process which enables the N-alkyl pyridinium salt to be recovered.

Thus according to our invention we provide a process for the separation of an N:N'-dialkyl-4:4'-bipyridylum halide salt from an N-alkyl pyridinium halide salt which comprises extracting a mixture of the solid halide salts with liquid chloroform.

It is especially preferred that the salts used for the purpose of our invention are the chlorides, though other halide salts may also be used if desired.

The solid salts may be obtained conveniently

by evaporating substantially to dryness the reaction mixture in which the salts are obtained. Anions other than halide anions are conveniently removed before this operation or replaced by halide anions using any convenient conventional technique, for example anion exchange or chemical metathesis. To improve the rapidity of separation the mixed salts may be broken up or ground to promote intimate contact with the chloroform.

The N:N' - dialkyl - 4:4' - bipyridylum salts may be in particular the N:N'-dimethyl-4:4'-bipyridylum salts but the process is also applicable to compounds containing higher alkyl substituents. Usually the N-alkyl pyridinium salt contains the same alkyl substituent as the N:N'-dialkyl-4:4'-bipyridylum salt, but this is not essential for the purpose of the present invention.

The procedure of extraction may be carried out in any convenient manner and using any conventional equipment or techniques for the purpose. Thus there may be used in particular a form of continuous extraction apparatus such as a Soxhlet apparatus, in which the mixture of solid salts is extracted with the solvent until no more solid is dissolved. Alternatively, the process may be carried out using a batch-wise technique in which the solid salts are digested repeatedly with the solvent. The mixture of salts and chloroform may be agitated to assist solution of the soluble component. The extraction may be carried out most conveniently at any temperature between ambient temperature and the boiling point of chloroform, particularly between 20°C and 62°C. Lower temperatures tend to give a slower extraction rate, while higher temperatures require operation under pressure and so are less convenient. The bipyridylum salt remains substantially undissolved and can then be recovered by drying the solid residue remaining

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PATENT SPECIFICATION

NO DRAWINGS

Inventors: JOHN PRESCOTT NEWPORT and REGINALD JOHN WILLIAM REYNOLDS

1,073,332



1,073,332

Date of filing Complete Specification: Jan. 25, 1966.

Application Date: March 11, 1965.

No. 10377/65

Complete Specification Published: June 21, 1967.

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Index at acceptance:—C3 P(4D3B1, 4D3B3, 4K4, 4T2D, 4T2E, 4T2X)

Int. Cl.:—C 08 f 27/08

COMPLETE SPECIFICATION

Quaternary Salts of Halogenated Polymers

5 We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to new polymeric materials, and more particularly to new vinyl quaternary ammonium polymers.

15 We have found that new and useful products can be made by quaternising vinyl α -halocarboxylate polymer with tertiary amine which consists of or contains bipyridyl.

20 Thus according to our invention we provide, as new polymeric material, the quaternary salt produced by treating a polymer of a vinyl ester of an α -halogenated aliphatic carboxylic acid with at least one bipyridyl, alone or in conjunction with at least one other tertiary amine.

25 The polymer of a vinyl ester of an α -halogenated aliphatic carboxylic acid may be a homopolymer or a copolymer, as desired. The α -halogenated aliphatic carboxylic acid from which the polymer is derived may be in particular one in which the halogen is chlorine, though those containing other halogens (for example bromine) which allow reaction to form a quaternary salt may be used if desired. Polyvinyl chloroacetate and chloroacetate copolymers are especially useful for the purpose of our invention. The 35 polymer may be made from the monomeric vinyl ester in known manner, for example by the action of a polymerisation initiator, for example azo-bis-isobutyronitrile or benzoyl peroxide. The polymerisation may be carried out conveniently in solution in an organic solvent (particularly in a ketone for example

methyl ethyl ketone) using approximately 0.02—2% of the polymerisation catalyst, based on the weight of monomer, and usually at about 40°—80°C in a medium conveniently containing about 50% by weight of the monomer. The molecular weight of the starting material may be selected according to the properties desired in the product and the uses for which the product is intended; materials in the molecular weight range 5000—50,000, for example, may be used.

50 The tertiary amine may be a bipyridyl alone and the bipyridyl may be in particular 2:2'-bipyridyl or 4:4'-bipyridyl, though other isomeric bipyridyls may also be used if desired. Mixtures of bipyridyls may also be used if desired. Alternatively, the tertiary amine may be a bipyridyl together with another tertiary amine, which may be aliphatic, alicyclic, or heterocyclic in nature, for example pyridine, morpholine, triethylamine or mixtures thereof.

65 The new products of our invention are formed by treating the polymer of a vinyl ester of a halogenated aliphatic carboxylic acid with the tertiary amine material, quaternisation occurring quite readily, and total or partial quaternisation may be achieved by varying the amount of tertiary amine used relative to the amount of polymer.

70 The halogen-containing polymer is usually soluble in ketones (for example methyl ethyl ketone), in nitrobenzene, or, at elevated temperatures, in hydrocarbon solvents such as benzene or toluene, and the bipyridyl (and any other tertiary amine used therewith) may conveniently be added to such solutions. It is convenient, for example, to use a solution containing a high proportion of the halogen-containing polymer to be quaternised (for example about 50% when the solvent permits, as in the case of methyl ethyl ketone). Gen-



PATENT SPECIFICATION

NO DRAWINGS

Inventors: DENNIS CHARLTON ALLPORT and JOHN HUBERT ENTWISLE

1,095,124

Date of filing Complete Specification (under Section 3 (3) of the Patents Act 1949): May 9, 1966.

Application Date: Feb. 10, 1965.

Application Date: April 2, 1965.

Complete Specification Published: Dec. 13, 1967.

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No. 4683/65.

No. 14105/65.

Index at acceptance: —C2 C(B4A2, B4H)

Int. Cl.: —C 07 d 29/10

COMPLETE SPECIFICATION

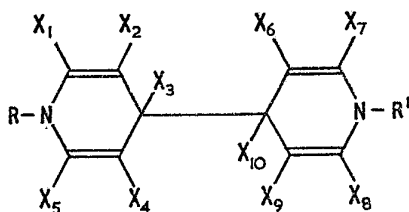
Bipiperidyl Derivatives and Processes for their Preparation

We IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1. a British Company. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of heterocyclic bases, and more particularly bipiperidyl derivatives.

According to the present invention we provide a process for the production of an N,N'-disubstituted-4,4'-bipiperidyl which comprises hydrogenating an N,N'-disubstituted tetrahydro-4,4'-bipyridyl wherein the substituents on the nitrogen atom are connected to the nitrogen atom by a non-acyl carbon atom.

The tetrahydrobipyridyl used as starting material may be in particular a compound of the structure



wherein R and R¹ are each organic derivatives containing a non-acyl carbon atom which is directly linked to the nitrogen atom of the pyridyl ring, and X₁—10 are each selected from the group consisting of hydrogen atoms, halogen atoms, nitro groups, —NH₂ groups and monovalent organic radicals and may be the same or different. By a "non-acyl carbon atom" we mean one that is not the carbon atom of an acyl (>C=O) group.

In their simplest form and giving rise to the most readily available class of compounds, R and R¹ are each hydrocarbon groups, particularly saturated and aromatically unsaturated groups such as alkyl, aryl, aralkyl or alkaryl (where alkyl includes cycloalkyl). Very useful chemical intermediates may be obtained where R and R¹ are each lower alkyl (that is, containing from 1 to 4 carbon atoms) and preferably methyl. However, R and R¹ may each be substituents wherein the carbon atom linked to the nitrogen atom is part of a chain containing atoms other than carbon, for example, N, O or halogen. Equally, the hydrogen atoms of the hydrocarbon groups may be replaced by other monovalent atoms or groups, commonly halogen and oxyhydrocarbon groups. It will be apparent that in some cases the structure of R and R¹ may be modified during the hydrogenation reaction, particularly where they contain readily reducible groups (e.g. unsaturated groups). However, it may be said that generally speaking whatever the nature of R and R¹ (whether or not they are modified during the hydrogenation process) they will not prevent the successful completion of our hydrogenation reaction although they may delay it or necessitate the use of more rigorous conditions.

Each X may be a hydrogen atom or a halogen atom or a group having the structure —NO₂ or —NH₂ or a monovalent organic radical, particularly one having the structure —Y, —OY, CO.Y, —SO₂.Y, —NHY, —NYY', —COOH, —COOY or —O.COY where Y and Y' are each monovalent hydrocarbon radicals or halogenated derivatives thereof. It may be said as a general principle that the nature of X will not prevent the successful completion of the hydrogenation process (even though it may itself be modified) although it

PATENT SPECIFICATION

NO DRAWINGS

1,129,511



1,129,511

Inventor: DENIS CHARLTON ALLPORT.

Date of filing Complete Specification: 13 January, 1966.

Application Date: 3 February, 1965.

No. 4685/65

Complete Specification Published: 9 October, 1968.

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Index at Acceptance:—C2 CB4A2.

Int. Cl.:—C 07 d 31/24.

COMPLETE SPECIFICATION

Production of a Pyridyl Piperidine

We IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of heterocyclic bases and in particular to the production of pyridyl piperidines.

We have found that although 4,4'-bipyridyl can be hydrogenated using a platinum catalyst in hydrochloric acid solution to form 4,4'-bipiperidyl, the hydrogenation can be made to yield 4-(4'-pyridyl) piperidine as the product if the acid content of the solution is restricted.

Thus according to our invention we provide a process for the manufacture of 4-(4'-pyridyl) piperidine which comprises hydrogenating 4,4'-bipyridyl in a mineral acid medium containing an amount of mineral acid which is less than 2 equivalents and preferably does not exceed 1 equivalent for each mole of the bipyridyl used.

The mineral acid may be in particular hydrochloric acid, though other mineral acids, for example hydrobromic acid, sulphuric acid or mixtures thereof, may be used if desired. Preferably the reaction medium may be an aqueous medium containing the mineral acid, though other solvents and/or diluents may be used as partial or complete replacement for the water if desired. As examples of such diluents there may be mentioned alcohols, for example methanol and ethanol, and aliphatic monocarboxylic acids for example acetic acid.

Hydrogenation may be carried out using a hydrated platinum oxide catalyst (Adams' catalyst) though other conventional forms of platinum hydrogenation catalysts may

also be used if desired.

We prefer to carry out the hydrogenation under conditions such that the concentration of 4,4'-bipyridyl in the reaction medium is in the range 5% to 30% by weight of the total reaction medium; and at a temperature in the range 20° to 150°C. The proportion of catalyst may be in the range of 0.1 - 5% based on the bipyridyl used; the hydrogenation occurring more rapidly when larger concentrations of catalysts in the range stated are used. The reaction may be carried out at atmospheric pressure or super-atmospheric pressure, as desired. The use of elevated pressures of hydrogen during reaction enable the reaction to be completed more quickly.

The proportion of mineral acid employed should preferably be 1 equivalent for each mole of 4,4'-bipyridyl employed since mixtures of products usually result when proportions other than this are employed in the range of above 0 to less than 2 equivalents of acid to 1 mole of bipyridyl. Thus, for example, use of 1.8 equivalents of mineral acid to 1 mole of bipyridyl will result in formation of a mixture of 4,4'-bipiperidyl and 4-(4'-pyridyl) piperidine.

The 4-(4'-pyridyl) piperidine may be isolated by filtration of the reaction medium to remove the catalyst, followed by treatment of the filtered solution with alkali, after which the product may be recovered by conventional means for example by solvent extraction, fractional distillation, or a combination of such techniques. The 4-(4'-pyridyl) piperidine product is a water-soluble hygroscopic white solid (m.p. 87°C) which is useful as an intermediate in chemical synthesis, and in particular can be alkylated to produce N-methyl-4-(4'-pyridyl) piperidine which is a useful basic catalyst in the production of poly-urethane foams.

[Price 4s. 6d.]

PATENT SPECIFICATION

1,130,551

NO DRAWINGS.

Inventor:—DENIS CHARLTON ALLPORT.

1,130,551



Date of filing Complete Specification: 13 Jan., 1966.

Application Date: 3 Feb., 1965. No. 4684/65.

Complete Specification Published: 16 Oct., 1968.

© Crown Copyright 1968.

Index at Acceptance:—C2 CB4A2.

Int. Cl.:—C 07 d 31/24.

COMPLETE SPECIFICATION.

Production of a Pyridyl Piperidine.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of heterocyclic bases and in particular to the production of pyridyl piperidines.

We have found that when 4,4'-bipyridyl is hydrogenated under selected conditions, hydrogenation does not proceed to completion to form 4,4'-bipiperidyl, but can be made to result in hydrogenation of only one of the pyridine nuclei so that the product is a pyridyl piperidine, in particular 4-(4'-pyridyl)-piperidine.

Thus according to our invention we provide a process for the production of 4-(4'-pyridyl)piperidine which comprises hydrogenating 4,4'-bipyridyl in a medium containing an aliphatic carboxylic acid.

The aliphatic carboxylic acid may be, for example acetic acid. If desired the aliphatic carboxylic acid, provided that it is liquid at the temperature of hydrogenation, may comprise substantially all of the reaction medium apart from the bipyridyl and any catalyst which is used. If desired, however, there may be present in addition to the aliphatic carboxylic acid some additional diluent, for example a hydrocarbon such as a petroleum ether or a cyclic saturated hydrocarbon such as cyclohexane, or water in limited amount.

The hydrogenation may be carried out using a hydrogenation catalyst and especially with a Raney nickel catalyst. Hydrogenation may be carried out at pressures and temperatures in the ranges of approximately 50

to 200°C. and up to 1000 atmospheres g., and is usually completed in a period of approximately 24 hours or less.

When hydrogenation is completed, as shown by cessation of the uptake of hydrogen, the desired product may be recovered from the reaction mixtures by conventional means for example by filtration (with the usual precautions) to remove the nickel catalyst followed by fractional distillation of the residue after liberating the free amine by treatment with a strong base for example sodium hydroxide or potassium hydroxide. The product is a solid (m.p. 87°C.) which can be isolated from the reaction mixture by extraction with benzene or petroleum ether after basifying to remove the acid present.

The process of our invention is surprising in that it was not to be predicted that only one of the pyridine nuclei of the bipyridyl would be hydrogenated and the expected product was bipiperidyl. The piperidyl pyridine product is a water soluble hygroscopic white solid (m.p. 87°C.) which is useful as an intermediate in chemical synthesis, and in particular can be alkylated to produce N-methyl(4-pyridyl)piperidine, which is a useful basic catalyst in the production of polyurethane foams.

The invention is illustrated but not limited by the following Example in which the parts and percentages are by weight.

EXAMPLE

4,4'-Bipyridyl (25 parts) was hydrogenated in 150 parts of glacial acetic acid using 2.5 parts of Raney nickel catalyst at 120°C. and 1500 p.s.i.g. hydrogen pressure. The green reaction solution was filtered and the filtrate was made strongly alkaline with aqueous

[Price 4s. 6d.]

PATENT SPECIFICATION

NO DRAWINGS

Inventor: CHARLES SHEPHARD

1087,052



1087,0

Date of filing Complete Specification: Dec. 4, 1964.

Application Date: June 8, 1964.

No. 23598/64.

Complete Specification Published: Oct. 11, 1967.

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Index at acceptance: —C2 C(B4A1, B4K)

Int. Cl.: —C 07 d 31/22

COMPLETE SPECIFICATION

Manufacture of 1,1'-Alkylene-2,2'-Bipyridylum Salts

ERRATUM

SPECIFICATION No. 1,087,052

Page 1, Heading, *Inventor:* for "CHARLES SHEPHARD" read "CHARLES SHEPHERD"

THE PATENT OFFICE
11th December 1967

ternary salts by interaction of ethylene dibromide with 2,2'-bipyridyl is known. Ethylene dichloride is less reactive, and usually requires an elevated pressure and temperature to make it react with 2,2'-bipyridyl at a speed adequate for commercial purposes, and under these conditions the reaction mixture is inconveniently corrosive. Consequently, although the expense of the bromide content of the bipyridylum salt (which does not itself contribute to the herbicidal effect of the product) can be avoided by use of the chloride, the manufacture of the chloride has not been found hitherto to be an attractive commercial proposition.

We have now found that 1,1' alkylene-2,2'-bipyridylum dihalide salts including 1,1'-ethylene-2,2'-bipyridylum dichloride can be obtained readily, even at atmospheric pressures, by bringing 2,2'-bipyridyl into reaction with certain mono-haloalkanols.

Accordingly this invention comprises a process for making a 1,1'-alkylene-2,2'-bipyridylum dihalide comprising reacting 2,2'-bipyridyl and a straight-chain mono-haloalkanol wherein an atom of chlorine or bromine and a hydroxyl group are attached to adjacent carbon atoms in the carbon chain of the alkanol molecule and either the atom of the halogen or the hydroxyl group is at-

ance not only because of the ease with which it can be made to react with the 2,2'-bipyridyl, but also because of the pronounced herbicidal properties of the resulting 1,1'-ethylene 2,2'-bipyridylum dichloride. The reaction between the haloalkanol and the bipyridyl takes place more readily in the absence of any substantial quantity of free acid and since haloalkanols on storage tend to develop acidity they may require purification before use.

The process may be carried out simply by heating the haloalkanol and the 2,2'-bipyridyl together. The reaction can be made to take place at different temperatures although those in the range of 130—170°C are preferred. Higher temperatures may be also used, although no particular advantage may be gained thereby. Lower temperatures may result in the reaction taking place at a rate which is too low to be convenient. The reaction can be carried out using the reactants dissolved in a solvent, which may be selected so as to boil at a temperature which is high enough to enable the reaction to take place quickly. Suitable solvents include water, polar organic solvents for example alcohols, ethers and nitrohydrocarbons, and non-polar organic solvents for example hydrocarbons and chlorinated hydrocarbons

[P]



PATENT SPECIFICATION

NO DRAWINGS

L.108.174

Inventor: JOHN EDWARD DOWNES

Date of filing Complete Specification: 23 April, 1965.

Application Date: 29 April, 1964.

No. 17785/64.

Complete Specification Published: 3 April, 1968.

© Crown Copyright 1968.

Index at acceptance:—C2 C(2A3, 2A5, 2A8, 2B53D3, 2B53G, 2B53M, 2B55, 2R15, 2R18); A5
E(1C4B2, 1C4B3, 1C4B4).

Int. Cl.:—C 07 d 31/40

COMPLETE SPECIFICATION

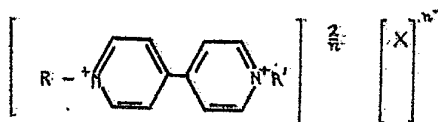
Bipyridylum Compounds and Herbicidal Compositions containing the same

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company of Imperial Chemical House, Millbank, London S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new 4,4'-bipyridylum compounds and to herbicidal compositions containing the same.

In recent times new herbicides have been discovered which contain as the active ingredient a bipyridylum compound comprising a cation which consists of a 4,4'-bipyridylum nucleus having a quaternising group attached to either or both of the nitrogen hetero atoms of the nucleus, and an anion. The compounds known hitherto are characterised by the fact that the quaternising group contains at least one carbon atom which forms a quaternising link with a nitrogen atom of the bipyridylum nucleus. We have now discovered new 4,4'-bipyridylum compounds wherein the quaternising group contains a nitrogen atom which forms a quaternising link with a nitrogen hetero atom of the 4,4'-bipyridylum nucleus.

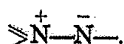
Accordingly, this invention provides a compound of the formula:—



where R is an unsubstituted amino group or a formamido group and R' is an unsubstituted amino group, a formamido group, a substituted or unsubstituted alkyl group, or a hydrogen atom, and X is an anion of valency n.

The invention includes compounds wherein one of the nitrogen hetero atoms is either unquaternised or bears a hydrogen atom or a group in which the quaternising link is between the nitrogen hetero atom and a carbon atom of the quaternising group. When the quaternising group forms a carbon to nitrogen link it may be an alkyl or substituted alkyl group having preferably from one to six carbon atoms. Substituted or unsubstituted methyl or ethyl groups are preferred. When the alkyl group is substituted it may bear as a substituent an alkoxy group, carbamoyl group, carbonylalkyl group, a carbonylalkoxy group, a carboxyl group or a hydroxy group.

The nature of the anion can vary considerably. Thus the anion may be bound by a covalent link to the 4,4'-bipyridylum nucleus as is the case when the nitrogen-containing quaternising group is itself negatively charged. In this case the compound has a nitrogen betaine structure. By the term nitrogen betaine we mean a compound which is represented in at least one of its canonical formulæ as containing the group



[Price 4s. 6d.]

Document is not available for IL23305 (A)



PATENT SPECIFICATION

NO DRAWINGS

1078,846

Inventors: JOHN THEODORE BRAUNHOLTZ and
CHARLES SHEPHERD

Date of filing Complete Specification: May 25, 1964.

Application Date: June 5, 1963.

No. 22319/63.

Complete Specification Published: Aug. 9, 1967.

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Index at acceptance:—C2 C(B4A1, B4K)

Int. Cl.:—C 07 d 39/00

COMPLETE SPECIFICATION

1,1'-Alkylene-2,2'-Bipyridylium Halides

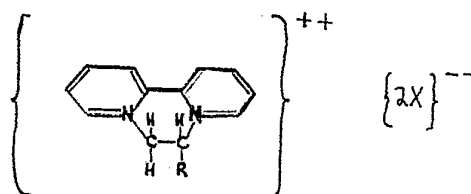
We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of 1,1'-alkylene-2,2'-bipyridylium halides.

The manufacture of herbicidal bis-quaternary dihalides by interaction of ethylene dibromide with 2,2'-bipyridyl is known. Ethylene dichloride is less reactive, and usually requires an elevated pressure and temperature to make it react with 2,2'-bipyridyl at a speed adequate for commercial purposes, and under these conditions the reaction mixture is inconveniently corrosive. Consequently, although the expense of the bromide content of the bipyridylium dihalide (which does not itself contribute to the herbicidal effect of the product) can be avoided by the use of the chloride, the manufacture of the chloride has not been regarded hitherto as an attractive commercial proposition.

We have now found that the formation of 1,1'-alkylene-2,2'-bipyridylium dihalides can be achieved very simply, without the necessity for the use of elevated pressure, by treating the 2,2'-bipyridyl with a mixture of a halogen and a 1-alkene. Suitable halogens are chlorine and bromine although the former is preferred.

Various alkenes may be used either singly or in the form of mixtures particularly those containing from 2 to 10 carbon atoms. The preferred alkene is ethylene in which case the reaction product will be an ethylene 2,2'-bipyridylium dihalide. When the reaction is carried out with alkenes containing more than two carbon atoms, substituted 2,2'-bipyridylium dihalides are formed, the most important members of which have the general formula



wherein R is an alkyl group and X is an atom of halogen.

We prefer to carry out the process using 2,2'-bipyridyl dissolved in a solvent which is preferably resistant to reaction with the halogen and boils at a temperature which is high enough to cause the reaction to proceed rapidly. The choice of solvent is also dependent on whether it is desired to maintain the reaction product in solution or for it to be deposited from the reaction mixture as it is formed. Suitable solvents can be either polar or non-polar and include water, alcohols, ethers, hydrocarbons and chlorinated hydrocarbons. The alkene used to form the dihalide may itself constitute the solvent. Especially good results have been obtained using a nitrohydrocarbon, for

[Price 4s. 6d.]

POOR QUALITY

PATENT SPECIFICATION

1,082,205

NO DRAWINGS.

Inventors:—JOHN THEODORE BRAUNHOLTZ and CHARLES SHEPHERD.

Date of filing Complete Specification: April 13, 1964.

Application Date: April 16, 1963. No. 14916/63.

Complete Specification Published: Sept. 6, 1967.

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1,082,205



Index at Acceptance:—C2 C(2A3, 2A5, 2A9, 2B36, 2B53D1, 2B53E, 2B53G, 2B53J2, 2B53K, 2R18, 2R19, 2R20, 2T16, 2T19, 2T22, 3A10B2D, 3A10B5A2, 3A10E4A4, 3A10E5A, 3A13A1A4, 3A13A1C, 3A14B3D, 3A14B5, B4A2, B4K); A5 E(1C4B2, 1C4B3, 1C4B4, 1C17).

Int. Cl.:—C 07 d 31/22 //A 01 n.

COMPLETE SPECIFICATION.

Manufacture of Herbicidal Materials Comprising 4,4'-Bipyridylum Diquaternary Salts.

ERRATA

SPECIFICATION NO. 1,082,205

Page 1, line 62, for "their" read "the"

Page 4, line 84, after "methyl" insert ")"

Page 4, line 85, after "hexyl" delete "chloroacetamithyl)"

Page 4, line 87, for "methoxyede" read "methoxyethyl"

Page 4, line 87, after "methoxyethyl" insert "chloroacetamide)"

Page 5, line 4, for "methyloperidin" read "methyloperidino"

THE PATENT OFFICE,
7th November 1967

D 94012/1

25 neat is evolved and consequently the re-
action is difficult to control. Furthermore,
the quaternary salts are obtained as solid
masses the handling of which is especially
difficult. With regard to the second process
30 bipyridylum quaternary salts are soluble in
water and they are generally used in the
form of aqueous solutions. When there-
fore an organic liquid is used in the quater-
nising process either the liquid must be re-
35 moved before converting the salt into a com-
position suitable for application as a herbi-
cide, or the liquid must be allowed to remain

and through their agency disquaternary salts 60
are obtainable in which the group attached
to their nitrogen atom can be the same or
different. The term bipyridyl used herein-
after shall be taken to include a quaternis-
able 4,4'-bipyridylum mono-quaternary 65
salt.

The nature of the quaternising groups
may vary considerably. However, all
quaternising agents the use of which is
comprehended within the scope of the in- 70
vention have the capacity of converting a
bipyridyl into a bipyridylum salt where a

PATENT SPECIFICATION

NO DRAWINGS

Inventors: FRANK RAYMOND BRADBURY and JAMES ADRIAN JARVIS

1.043.356



1.043.356

Date of filing Complete Specification: Jan. 28, 1964.

Application Date: Feb. 13, 1963.

No. 5900/63.

(Patent of Addition to No. 996570 dated Feb. 18, 1963).

Complete Specification Published: Sept. 21, 1966.

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Index at acceptance:—C2 C(B4A2, B4J)

Int. Cl.:—C 07 d 31/16

COMPLETE SPECIFICATION

Purification of Bipyridyls

5 We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a purification process, and more particularly to a process for the removal of terpyridyl impurities (especially 2:2',6':2''-terpyridyl) from bipyridyls.

15 The methods available for the production of bipyridyls, particularly from pyridine, usually give rise to mixtures of isomers. In addition, such mixtures often contain tarry and polymeric by-products and higher polypyridyls, of which 2:2',6':2-terpyridyl is especially troublesome on account of its high toxicity. Consequently, it is highly desirable that efficient methods should be available for freeing bipyridyls from this terpyridyl.

25 Separation of bipyridyls and terpyridyls can be achieved by distillation but this is not a convenient or satisfactory method because they are high-boiling materials. Distillation is particularly inconvenient when the bipyridyls are produced by a process which provides them in aqueous solution. Also, in view of the small proportions of terpyridyl concerned, methods based on crystallisation or solubilities are not sufficiently effective for commercial use.

35 We have now found that the desired purification can be achieved by solvent extraction of the bipyridyls from an aqueous acid medium in the presence of a metal compound which can form a complex with the terpyridyl, especially ferrous iron, the terpyridyl being thus held in the aqueous phase. This has the advantage, not only of enabling the

toxic terpyridyl to be removed from the bipyridyl, but also of eliminating toxic material in an aqueous stage rather than accumulating a very dangerous residue in a still boiler. We also find the added advantage that the toxicity of the terpyridyl itself is reduced by conversion to iron complex. 45

Thus according to our invention we provide a process for the removal of terpyridyl impurity from a bipyridyl which comprises contacting the impure bipyridyl with a substantially water-immiscible organic solvent and an aqueous acid medium containing at least one compound of nickel, cobalt, zinc, or iron and thereafter separating the organic solvent phase, which contains the bipyridyl. We prefer to use ferrous iron. 50 55

The process is especially applicable to the purification of 4:4'-bipyridyl. Mixtures of crude bipyridyls in which the 4:4'-isomer predominates and which are especially well suited to treatment by our process are those made from a magnesium-pyridine interaction product (for example by oxidation) as the bipyridyls made by this route usually contain significant amounts of terpyridyl. 60 65

The substantially water-immiscible organic solvent may be any organic solvent in which the bipyridyls are soluble, and may be in particular a hydrocarbon for example toluene or benzene, or a chlorinated hydrocarbon for example trichloroethylene or perchloroethylene. Mixtures of solvents may be used if desired. 70 75

The aqueous acid medium preferably has a pH in the range 5 to 6, as recovery of the purified bipyridyl is best within this range. Lower pH may be used if desired, but retention of bipyridyls in the aqueous phase can then become excessive. Higher pH tends to cause formation of precipitates, for example of ferric hydroxide, which can inter- 80

[P: _____.]

PATENT SPECIFICATION

NO DRAWINGS

Inventors: RONALD FREDERICK HOMER and JOHN EDWARD DOWNES

1.070.504



1.070.504

Date of filing Complete Specification: Dec. 23, 1963.

Application Date: Jan. 31, 1963.

No. 49145/62.

Complete Specification Published: June 1, 1967.

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Index at acceptance: —A5 E(1C4B1, 1C4B3, 1C4B4); C2 C(2B53D1, 2B53E, 2B53G, B4A2, B4K)

Int. Cl.: —A 01 n 19/02//C 07 d

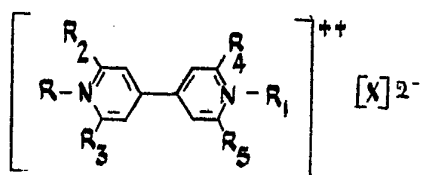
COMPLETE SPECIFICATION

Herbicidal Compositions

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to herbicidal compositions containing as active ingredient a substituted bipyridylium salt and to processes of combating weeds using them.

The invention provides herbicidal compositions comprising as active ingredient a 4,4'-bipyridylium quaternary salt wherein each nitrogen atom bears an aliphatic group and at least one of the four ring carbon atoms which are adjacent a nitrogen atom in the pyridine nuclei bears as a substituent an alkyl group containing from 1—4 carbon atoms; and a carrier for the active ingredient, said carrier comprising an inert solid diluent, or a liquid diluent comprising a wetting agent. The compositions preferably comprise a quaternary salt wherein the substituent alkyl group is a methyl group and it is further preferred to employ active ingredient a quaternary salt in which each pyridine nucleus bears a substituent methyl group on a ring carbon atom adjacent a nitrogen atom. The invention further provides, herbicidal compositions comprising as active ingredient a compound of the formula:



wherein R and R₁, which may be the same or different, are each alkyl groups containing from 1—4 carbon atoms, R₂, R₃, R₄ and R₅ are groups which include at least one methyl group the remainder being either methyl groups or hydrogen atoms and X is a divalent anion or two monovalent anions; and a carrier for the active ingredient, said carrier comprising an inert solid diluent or a liquid diluent comprising a wetting agent. R and R₁ are preferably methyl or ethyl groups.

The anionic part of the salt may comprise for example chloride, bromide or iodide ions although [X]²⁻ may also comprise a single divalent ion. The choice of anion depends to a large extent upon the solubility of the respective salts in water and upon the ease with which the salts can be prepared.

Symmetrical compounds of the invention can be obtained by reacting the appropriate ring—substituted 4,4'-dipyridyl with a suitable quaternising agent. Other compounds can be prepared by a similar process in which a 1-substituted -4-(4'-pyridyl)-pyridinium salt is quaternised with a suitable quaternising agent, the pyridinium salt being chosen so that its 1-aliphatic substituent is on of the aliphatic substituents required in the bipyridylium salt, and the quaternising agent is such that it introduces the required second aliphatic substituent and anion. The reaction in some instances can be carried out simply by heating the reactants together, but it is generally more convenient, especially where the process is carried out on a large scale, to have the reactants in solution or suspension in a suitable solvent or diluent.

The compositions may be in the form of concentrated compositions which is the form in which they are transported more conveniently because they contain a high proportion of the salt with a minimum of bulk. In general these compositions are diluted before

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PATENT SPECIFICATION

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NO DRAWINGS.

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COMPLETE SPECIFICATION.

Catalytic Process for the Production of Organic Bases.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a catalytic process for the manufacture of organic bases, and more particularly for the manufacture of organic bases from tetrahydrofurfuryl alcohol and ammonia.

It is known that tetrahydrofurfuryl alcohol and ammonia can be made to react together at elevated temperatures in the presence of mixtures of alumina and chromium oxide to form pyridine.

We have now found that the course of the reaction can be altered, so that different organic bases are formed, by using a finely divided palladium catalyst. The organic bases thus formed appear to correspond to the molecular formula $C_{15}H_{27}N_3$. The product is usually a mixture, the principal components of which are believed to be the various isomeric polycyclic amine products known as tripiperideines and described by Schöpf et al (Annalen der Chemie 559, (1948), page 1; Chem. Ber. 84, 690—9 (1951)).

Thus according to the present invention we provide a process for the manufacture of organic bases which comprises contacting a mixture of tetrahydrofurfuryl alcohol and ammonia at elevated temperatures with finely divided palladium as catalyst.

The palladium catalyst may be made in conventional manner and is most conveniently used on a support or carrier, for example alumina. The proportion of pal-

ladium metal on the carrier need not be very high, and a catalyst containing as little as 0.04% by weight of palladium metal on alumina is very suitable for use in our process.

The proportions of tetrahydrofurfuryl alcohol and ammonia to be used are conveniently within the range of 1 to 10 moles of ammonia for each mole of tetrahydrofurfuryl alcohol. Larger proportions of ammonia may cause inconvenience or expense, through loss or need for recovery, and smaller proportions tend to lower the efficiency of conversion of the tetrahydrofurfuryl alcohol to bases, but such proportions may be used if desired.

We prefer to add hydrogen to the mixture of tetrahydrofurfuryl alcohol and ammonia, as this tends to minimise undesired side-reactions. The proportion of hydrogen is preferably between 1 and 10 moles for each mole of tetrahydrofurfuryl alcohol. Larger proportions may be used if desired, but these tend to introduce problems of condensation and recirculation with the large volumes of gas or vapour then employed. If desired, inert gases, for example nitrogen, may also be added to the mixture.

The reaction temperatures is preferably within the range 200° C. to 500° C. Higher temperatures tend to cause an increase in the loss of material by carbonisation and lower temperatures tend to give a lower conversion efficiency, but may be used if desired.

It is usually most convenient to operate the process by vapourising tetrahydrofurfuryl alcohol at the desired rate, mixing the vapour with the desired proportion of ammonia (and hydrogen, when this also is used), heating the mixture and passing it

[Price 4s. 6d.]

Price 25p